

LIQUID IMMISCIBILITY IN A LUNAR PLUTONIC SETTING AND THE EVOLUTION OF KREEPY RESIDUAL MELTS; BRADLEY L. JOLLIFF AND CHRISTINE FLOSS, Department of Earth and Planetary Sciences and the McDonnell Center for the Space Sciences, Washington University, St. Louis, MO 63130. (blj@levee.wustl.edu)

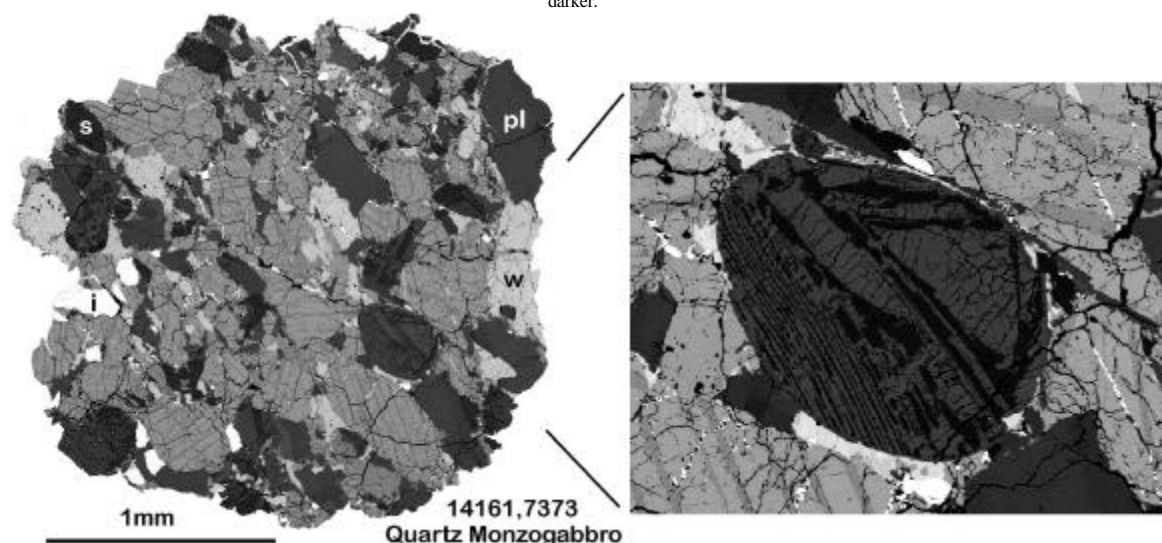
Introduction. Liquid immiscibility has been proposed as a process that might have produced lunar granite and separated felsic and mafic components of lunar residual melts (K-frac and REEP-frac, [1,2]). One or the other of these components has been inferred to be the agent of metasomatism [1,2] or autometasomatism [3], or to have been an important assimilant at depth in the Moon's crust. Textures reflecting liquid immiscibility have been observed in the late stage, iron-rich mesostasis of mare basalts [4], and immiscibility has been produced experimentally in Fe-rich KREEP-like compositions [5]; however, only one lunar sample yet studied shows incontrovertible petrographic evidence for liquid immiscibility in a plutonic assemblage. Sample 14161,7373, a whitlockite-rich "quartz monzogabbro," was originally described by [6] and, in an ion-microprobe study of its phosphates, Jolliff et al. [3] gave a model for its late-stage crystallization history. Important unanswered questions are how concentrated in incompatible elements lunar residual melts were at the time of immiscible liquid separation, and how effective such separated melts might have been as metasomatizing agents in the lunar crust. In this abstract, we present the results of ion-microprobe analyses of pyroxenes and feldspars in 14161,7373. For a sample whose bulk assemblage has REE concentrations at $\sim 5\text{--}6 \times$ KREEP levels, the silicates have surprisingly low REE concentrations. The high bulk REE concentrations are the result of a high proportion of whitlockite, probably an excess (i.e., a whitlockite cumulate). We conclude that the REE distribution between minerals resulted from relatively low-T (900°C) equilibration of the final assemblage.

Sample Description. Sample 14161,7373 was discovered during an INAA survey of rocklets in Apollo 14 soils [7]. It is a relatively coarse-grained fragment of a larger rock, and although strongly shocked and fractured, it retains

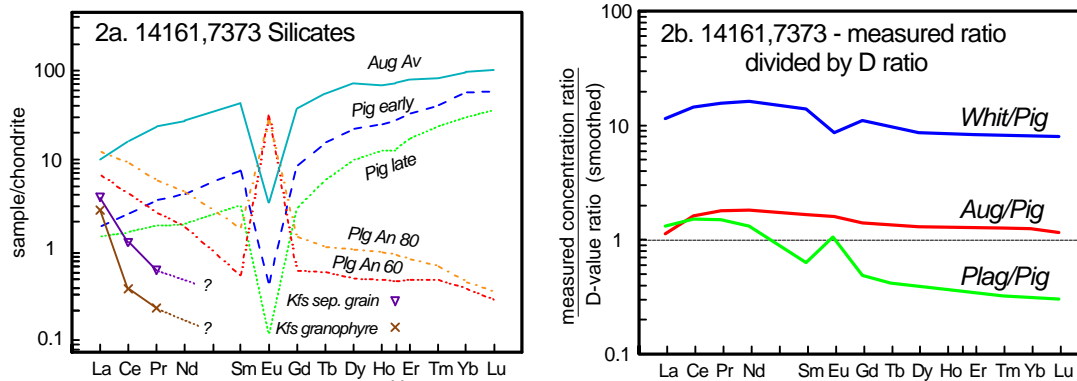
relict igneous texture (Fig. 1a). Grain sizes are coarse: pigeonite up to 600 μm , plagioclase, 500 μm , whitlockite, 500 μm , K-feldspar, 100 μm , silica, 200 μm , and granophyric intergrowths of K-feldspar and silica, 250 μm . Major element compositions of the coarse pyroxenes are quite uniform ($\text{En}_{37}\text{Fs}_{56}\text{Wo}_7$, $\text{En}_{30}\text{Fs}_{31}\text{Wo}_{39}$), indicating that, for major elements, they are well equilibrated [5]. Plagioclases retain some compositional variation, ranging from coarse calcic grains ($\text{An}_{82}\text{Ab}_{17}\text{Or}_1$) to fine, interstitial, more sodic grains ($\text{An}_{57}\text{Ab}_{40}\text{Or}_3$). Barian K-feldspar compositions average $\text{Or}_{83}\text{Ab}_{12}\text{Cn}_{3.5}\text{An}_{1.7}$. Pyroxenes are mostly uninverted pigeonite with medium augite exsolution lamellae (typically $\sim 10 \mu\text{m}$) on 001. Separate augite grains are also present. Silica is present in several forms, identified by laser Raman spectroscopy: amorphous, with very fine-grained patches of quartz, and some "relict" cristobalite. In an unusual texture, several separate grains of silica contain abundant troilite blebs, and thin troilite stringers fill an early set of fractures. Textures that reflect unambiguous liquid immiscibility are perfectly preserved; one of these is an egg-shaped granophyre $\sim 250 \mu\text{m}$ across (Fig. 1-right). Another occurs in the shape of an elongate tear drop.

Ion-Microprobe Results. We measured the REE concentrations and other elements with the modified Cameca 3-f ion microprobe at Washington University. We analyzed coarse-grained exsolved pigeonite within both the low-Ca regions as well as a high-Ca lamella. We also analyzed a separate, exsolved augite grain as well as a small grain that is not exsolved. We analyzed coarse, relatively calcic plagioclase grains (An_{80}) and a smaller, more albitic interstitial grain (An_{60}), and we analyzed K-feldspar within a granophyric intergrowth (Fig. 1-right) and in a separate grain. The results are plotted relative to chondrites in Fig. 2a. Augite has, among the silicates, the highest REE abundances, and

Figure 1. Backscattered-electron images of 14161,7373. The darkest phase is silica (s); feldspars are dark gray (pl=plag), pyroxenes are medium gray with augite slightly darker; whitlockite (w), light gray, and ilmenite (i) and zircon, bright. Troilite is very bright, forming tiny grains in silica-rich masses and thin stringers filling fractures. In the granophyric "egg", K-feldspar is lighter, silica darker.



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concentrations in all three measured spots are similar. Concentrations of REE in pigeonite vary by about a factor of two; we interpret these as an early (high) to late (low) crystallization sequence. Plagioclase REE contents also span a range of about a factor of two, and the small, relatively albitic (presumably late) grain has the lowest REE concentrations. The K-feldspar grains have very low concentrations; because of interference from Ba ions, we could reliably measure only the LREE and Y. In both pigeonite and plagioclase, the grains we infer to have formed late in the crystallization sequence have higher La/Sm and lower Gd/Lu.

Discussion. Given that this sample retains unambiguous igneous texture and is demonstrably monomict [6,8], we might be tempted to use experimental distribution coefficients to estimate REE concentrations in the melt that would have been in equilibrium with the pyroxenes and feldspars that we analyzed. However, when we do this, we find that each mineral group points to a different melt composition. This is illustrated in Fig. 2b, which plots the measured concentration ratios divided by the D-value ratios. (To construct Fig. 2b, we assumed that a pigeonite host and augite lamella pair that we analyzed are in equilibrium for REEs, and we used this relationship to calculate REE D values for pigeonite based on augite D values calculated according to [9] (Wo_{39}). These pigeonite D values are significantly higher than those we would estimate using [9].) Figure 2b, where we also compare whitlockite [3], shows that measured REE concentrations in whitlockite are much higher, relative to pigeonite, than we would expect based on the D values (mainly from [9,10,3]). Likewise, concentrations of Sm and HREEs in plagioclase are lower than expected. Calculated equilibrium liquids would range from somewhat less than KREEP levels (plagioclase) to 1–2 \times KREEP levels (pigeonite, augite) to $\sim 8 \times$ KREEP levels (whitlockite). However, as shown by [3] for whitlockite, the concentrations levels in this rock relate to mass balance and mineral-mineral distribution coefficients and the final degree of equilibration of the assemblage. Furthermore, distribution coefficients are temperature dependent [11,12] such that $D(\text{REE})\text{-plag/melt}$ decrease and $D(\text{REE})\text{-pyroxene/melt}$ increase at lower T than those under which the most relevant published D values were obtained. We do not know about $D(\text{REE})\text{-whit/melt}$, but we suspect they increase at lower T. In this assemblage, the major elements indicate that the pyroxenes equilibrated to $\sim 900^\circ\text{C}$ [13].

It is difficult to estimate directly the REE concentrations of “parent” melt from which this assemblage crystallized. It may have been only as high as $1 \times$ KREEP if the cores of the coarse silicates faithfully record the melt from which they crystallized, or as high as $4 \times$ KREEP for melt in equilibrium with whitlockite [3]. In any case, the variations between early and late crystallizing silicates reflect co-crystallization of whitlockite, which caused a bowing downward of REE patterns and general depletion of REEs, especially the MREE, in late plagioclase and pigeonite. Barian K-feldspars appear to record an extreme depletion of the MREE, consistent with their formation from late-stage residual melt, in some cases as part of granophyric segregations of felsic material whose textures indicate that the felsic material separated from mafic residual melt by immiscibility prior to their solidification. In this assemblage, whitlockite crystallization *preceded* liquid immiscibility.

The unusual texture of silica containing dispersed sulfide blebs records another intriguing late-stage separation. Silica within granophyric intergrowths is free of troilite inclusions, whereas separate silica-rich masses contain as much as 5% of other components besides SiO_2 , mainly troilite. Late-stage fractures throughout the assemblage are filled with troilite; these coupled observations suggest a very late stage separation of immiscible Fe-S-rich liquid from the highly siliceous fraction of residual melt.

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